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2. Patent application number (The Patent Office will fill in this part)	0224379.8		21 OCT 2002
3. Full name, address and postcode of the or of each applicant ( <u>underline all surnames</u> )	Givaudan SA Chemin de la Parfumerie 5 1214 Vernier Switzerland		
Patents ADP Number (if you know it)	8408031001		
If the applicant is a corporate body, give the country/state of its incorporation	Switzerland		
4. Title of the Invention	Improvements in or related to organic compounds		
5. Name of your agent (if you have one)			
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Patents ADP number (if you know it)	8447815001		
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:)	yes		
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Colin Brown (office time) Tel. No: 01/784417721

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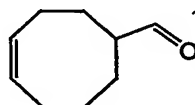
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Improvements in or related to organic compounds

This invention relates to substituted cyclooct-3-enes having agrestic, natural, and floral, green, woody odour notes, their manufacture, and to fragrance compositions containing them.

Substituted cyclooctenes have been described in the literature, for example the German patent publication DE 19814913 A1 discloses cyclooctene aldehydes, such as cyclooct-4-en aldehyde (1) possessing an odour note described to be comparable with the odour of fresh harvest potatoes.

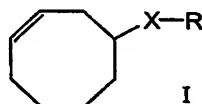


(1)

Whereas the odour notes imparted by cyclooct-4-en aldehyde (1) may be interesting in their own right, in the fragrance industry there is always an ongoing demand for new compounds that enhance, or improve on odour notes or impart new odour notes.

Surprisingly, we have now found certain monosubstituted cyclooct-3-enes structurally similar to (1), but which possess characteristically different odour notes which are described as agrestic and thujone-like, and floral, green, woody odour notes.

In a first aspect the invention refers to the use of a compound of formula I as fragrance,



I

wherein X is carbonyl, or -(CHOH)- ; and

R is methyl or ethyl, or linear or branched C3 to C5 alkyl, such as *i*-propyl, *n*-propyl, *n*-butyl, *sec*-butyl, *tert* butyl, *n*-pentyl, *sec*-pentyl, and *tert*-pentyl; or

R is vinyl or linear or branched C3 to C5 alkenyl, such as propen-1-yl, propen-2-yl, allyl, but-1-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, and pentenyl.

The compounds according to the present invention may contain one or more chiral centres and as such may exist as a mixture of stereoisomers, or they may be resolved as isomerically pure forms. Resolving stereoisomers adds to the complexity of manufacture and purification of these compounds and so it is preferred to use the compounds as mixtures of their stereoisomers simply for economic reasons. However, if it is desired to prepare individual stereoisomers, this may be achieved according to methodology known in the art, e.g. preparative HPLC and GC or by stereoselective syntheses.

- 10 Particular preferred compounds of formula I are 1-cyclooct-3-enylethanone, 1-cyclooct-3-enylpropan-1-one, 1-cyclooct-3-enyl-2-methylpropan-1-one and 1-cyclooct-3-enylpropan-1-ol.

The compounds according to the present invention may be used alone or in combination with known odourant molecules selected from the extensive range of natural and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture with one or more ingredients or excipients conventionally used in conjunction with odourants in fragrance compositions, for example carrier materials, and other auxiliary agents commonly used in the art.

The following list comprises examples of known odourant molecules which may be combined with the compounds of the present invention:

- 25 natural products: tree moss absolute, basil oil, tropical fruit oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil, wormwood oil, lavender oil, rose oil, jasmin oil, ylang-ylang oil.

alcohols: farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol, (Z)-hex-3-en-1-ol, menthol,  $\alpha$ -terpineol.

aldehydes: citral,  $\alpha$ -hexyl cinnamaldehyde, Lilial, methylionone, verbenone, nootkatone, geranylacetone.

esters: allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, cis-3-hexenyl isobutyrate, cis-3-hexenyl salicylate, linalyl acetate, methyl dihydrojasmonate, styralyl propionate, vetiveryl acetate, benzyl acetate, geranyl acetate.

lactones:  $\gamma$ -undecalactone,  $\delta$ -decalactone, pentadecanolide, 12-oxahexadecanolide.

acetals: Viridine (phenylacetaldehyde dimethylacetal).

other components often used in perfumery: indole, p-mentha-8-thiol-3-one, methyleugenol, eugenol, anethol.

The compounds of the present invention may be used in a broad range fragrance applications, e.g. in any field of fine and functionary perfumery, such as perfumes, household products, laundry products, body care products and cosmetics. The compounds can be employed in wide ranging amounts depending upon the specific application and on the nature and quantity of other odourant ingredients, that may be for example, from about 0.001 to about 20 weight percent. In one embodiment compounds may be employed in a fabric softener comprising in amount of about 0.001 to 0.05 weight percent. In another embodiment compounds of the present invention may be in alcoholic solution in amounts of about 0.1 to 20 weight percent, more preferably between about 0.1 and 5 weight percent. However, these values should not be limiting on the present invention, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.

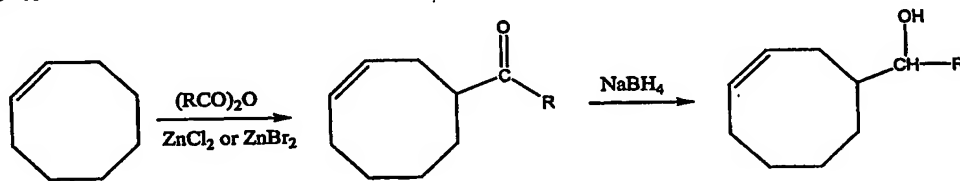
The compounds of the present invention may be employed into the fragrance application simply by direct mixing the fragrance composition with the fragrance application, or it may be in a previous step entrapped with an entrapment material such as for example polymers, capsules, microcapsules and nanocapsules, liposomes, precursors, film formers, absorbents such as for example by using carbon or zeolites, cyclic oligosaccharides and mixtures thereof, and then mixed with application.

Whereas the compound of formula I wherein X represents a carbonyl group and R is methyl is known, the olfactive properties have not been previously described.

Thus, in a second aspect the invention provides a compound of the formula I,  
 5 wherein X is carbonyl, or  $-(\text{CHOH})-$ ; and  
 R is methyl or ethyl, or linear or branched C3 to C5 alkyl, such as *i*-propyl, *n*-propyl, *n*-butyl, *sec*-butyl, *tert* butyl, *n*-pentyl, *sec*-pentyl, and *tert*-pentyl; or  
 R is vinyl or linear or branched C3 to C5 alkenyl, such as propen-1-yl, propen-2-yl, allyl, but-1-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, and pentenyl;  
 10 provided that when X is carbonyl, R is not methyl.

Compounds of formula I may be prepared by the reaction of olefins with an appropriately substituted carboxylic acid, well known to a person skilled in the art and described for example by Schellhammer (Methoden der Organischen Chemie (Houben-  
 15 Weyl), 1973, Band VII/2a, pages 447 – 460) herein incorporated by reference, starting from cyclooctene by acylation with the appropriately substituted carboxylic acid. The resulting ketones may be reduced to give further compounds of formula I as shown in scheme 1.

20 Scheme 1:



Further particulars as to reaction conditions are provided in the examples.

25

There now follows a series of examples that illustrate the invention.

#### Example 1: 1-cyclooct-3-enylethanone

To cyclooctene (300 g, 2.73 mol) were added acetic anhydride (556 g, 5.45 mol) and zinc chloride (30 g, 0.22 mol). The reaction mixture was warmed to 90°-95°C within 30  
 30 min., stirred at that temperature during 7.5 hours, cooled to 60°C, and treated with

caution, within 10 min., with water (400 ml). The resulting mixture was heated at 100°C during 3 h., cooled to 25°C, and extracted with hexane (3 x 300 ml). The combined organic phases were washed with aq. sat. NaCl soln. (800 ml), aq. sat. NaHCO<sub>3</sub> soln. (800 ml), aq. sat. NaCl soln. (400 ml), and dried with Na<sub>2</sub>SO<sub>4</sub> (200 g). Filtration and  
 5 evaporation of the solvent led to 375 g of crude material which was distilled under vacuum with a short-path Vigreux column. After collecting the unreacted cyclooctene (65 g, 21.7%) at 40-50°C/100 mbar, the fractions distilling at 110°C/24 mbar were collected (144 g) and redistilled using a microdistillation column (20 x 1.5 cm, filled with 3 x 3 mm rolled wire netting) to give 110 g of 1-cyclooct-3-enylethanone (34% based on  
 10 the reacted cyclooctene, 109°C/20 mbar) as colourless oils.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  1.40-1.85 (*m*, 6H), 2.05-2.16 (*m*, 1H), 2.16 (*s*, Me), 2.16-2.30 (*m*, 2H), 2.38-2.47 (*m*, H-C(2)), 2.49-2.57 (*m*, H-C(1)), 5.60 (*dd*, *J* = 8.2, 18.5, H-C(3)), 5.73 (*dd*, *J* = 8.0, 18.3, H-C(4)). <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>):  $\delta$  24.19 (*t*, C(7)),  
 15 25.58 (*t*, C(5)), 26.13 (*t*, C(2)), 27.12 (*t*, C(8)), 28.08 (*q*, Me), 28.96 (*t*, C(6)), 52.66 (*d*, C(1)), 127.38 (*d*, C(3)), 131.48 (*d*, C(4)), 211.20 (*s*, CO). MS (EI): 152 (15), 137 (7), 134 (15), 119 (10), 109 (35), 94 (21), 79 (36), 67 (100), 55 (37), 43 (100). IR:  $\nu_{\max}$  3016, 2927, 2855, 1708, 1666, 1466, 1467, 1352, 1241, 1165, 1120, 959, 755, 706 cm<sup>-1</sup>.

20 Odour description: agrestic, armoise, wormwood, thujone, natural.

#### Example 2: 1-cyclooct-3-enylpropan-1-one

Obtained according to the experimental procedure of Example 1 from cyclooctene (150 g, 1.36 mol), propionic anhydride (354 g, 2.72 mol) and zinc bromide (30.6 g, 0.14 mol)  
 25 in 27% yield. Boiling point 60°C/80 mbar.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  1.04 (*t*, *J* = 7.3, Me), 1.40-1.80 (*m*, 6H), 2.03-2.12 (*m*, 1H), 2.17-2.27 (*m*, 2H), 2.39-2.58 (*m*, H-C(2), CH<sub>2</sub>CO, H-C(1)), 5.60 (*dd*, *J* = 8.1, 18.5, H-C(3)), 5.73 (*dd*, *J* = 8.4, 18.4, H-C(4)). MS (EI): 166 (18), 137 (16), 109 (41), 94 (19), 79  
 30 (25), 67 (100), 57 (83), 41 (34), 29 (39). IR:  $\nu_{\max}$  3017, 2928, 2855, 1708, 1669, 1464, 1413, 1375, 1115, 973, 754, 705 cm<sup>-1</sup>.

Odour description: fruity, banana, tagete.



Example 3: 1-cyclooct-3-enyl-2-methylpropan-1-one

Obtained according to the synthetic procedure of Example 1 from cyclooctene (150 g, 1.36 mol), isobutyric anhydride (430.3 g, 2.72 mol) and zinc bromide (30.6 g, 0.14 mol) in 33% yield. Boiling point 85°C/80 mbar).

5

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ 1.08 (t, J = 7.0, Me), 1.39-1.78 (m, 6H), 2.02-2.29 (m, 3H), 2.42 (dt, J = 8.8, 13.6, H-C(2)), 2.62-2.70 (m, H-C(1)), 2.79 (h, J = 6.9, H-CMe<sub>2</sub>), 5.60 (dd, J = 8.4, 18.4, H-C(3)), 5.74 (dd, J = 8.0, 18.4, H-C(4)). MS (EI): 180 (17), 165 (1), 137 (21), 119 (6), 109 (59), 94 (9), 81 (13), 79 (14), 71 (32), 67 (100), 55 (29), 53 (10), 43 (63), 39 (20), 27 (14). IR: ν<sub>max</sub> 3017, 2967, 2928, 2857, 1701, 1666, 1466, 1382, 1051, 1004, 756, 735 cm<sup>-1</sup>.

10

Odour description: fruity, green.

15 Example 4: 1-cyclooct-3-enylpropan-1-ol

1-cyclooct-3-enylpropan-1-one (84.0 g, 0.5 mol) was slowly added to a suspension of sodium borohydride (11.9 g, 0.3 mol) in ethanol (330 ml) at 0°C (ice bath) and stirring continued at room temperature for 4 h. The reaction mixture was poured into ice-cold 2N HCl (500 ml) and extracted with MTBE (2 x 200ml). After washing with brine (3 x 200 ml), drying (MgSO<sub>4</sub>) and evaporation of solvents, the yellowish oily residue (86.6 g) was distilled over a 20 cm Widmer column (66-80°C/0.7-0.8 mbar) to give 69.2 g of 1-cyclooct-3-enylpropan-1-ol (colourless oil, 68% yield). It consisted of >90% of 1:1 mixture of two diastereomeric racemates of 1-cyclooct-3-enylpropan-1-ol. An analytical sample was purified by flash chromatography (hexane/MTBE 3:1).

20

25

R<sub>f</sub> 0.51. <sup>1</sup>H-NMR (200MHz, CDCl<sub>3</sub>): δ 0.95 and 0.97 (2t, J = 7.4 and 7.3, 3H), 1.22-1.76 (m, 10H), 2.02-2.27 (m, 4H), 3.32-3.46 (m, 1H), 5.54-5.70 (m, 2H). <sup>13</sup>C-NMR: diast. rac. A: δ 10.1 (q), 24.6 (t), 25.4 (t), 26.4 (t), 27.1 (t), 28.5 (t), 29.1 (t), 45.2 (d), 77.1 (d), 128.9 (d), 130.4 (d); diast. rac. B: δ 10.2 (q), 24.2 (t), 25.3 (t), 26.8 (t), 26.9 (t), 27.8 (t), 28.9 (t), 45.2 (d), 77.1 (d), 128.9 (d), 130.3 (d). MS (EI): 168 (M<sup>+</sup>, 2), 150(16), 139(16), 121(76), 109(25), 107(26), 93(31), 82(28), 81(35), 79(49), 67(100), 59(50), 57(41), 55(43), 41(55). IR (neat): ν<sub>max</sub> 3359, 2925, 2856, 1466, 1106, 968, 755, 705 cm<sup>-1</sup>.

30

Odour description: cassie, mimosa, green, moss, natural, forest, fatty

Example 5: A fragrance composition for a soap :

	<u>compound/ingredient</u>	<u>parts by weight 1/1000</u>
5	Civette GIVCO 208*	1
	Ethyl vanilline	1
	cis-Jasmone	1
	Castoreum GIVCO 116*	2
	Galbanum GIVCO 121*	2
10	Aldehyde C110 Undecylic	3
	Cyclal C	3
	Petitgrain essential oil Paraguay	3
	Iso Butyl Quinoleine (at 10% in DPG)	3
	Evernyl	4
15	Dimethyl Anthranilate	4
	Givescone	5
	Dimethyl Octenone	6
	Labienoxime (1%/CQS)	6
	Tangerinol	6
20	Sandalwood GIVCO 203*	6
	Florhydral	7
	Allyl Amyl Glycolate	8
	Romarin essential oil	8
	Velvione	10
25	Coumarine	10
	Okoumal	10
	Thibetolide	10
	Oxyoctaline Formate	15
	Isoraldeine 95	15
30	Gaiacwood essential oil	20
	Lemon essential oil California	20
	Patchouli essential oil	20
	Amyl Salicylate	20
	Benzyl Acetate	30

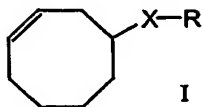
	Geranodyle	35
	Citronellol	40
	Lavandin Grosso essential oil	50
	Alpha Hexyl Cinnamic Aldehyde	80
5	Dihydro Myrcenol	130
	Bergamote GIVCO 104*	200
	Dipropylene Glycol	203
	1-cyclooct-3-enylethanone (compound Example1)	3
		<hr/>
10		1000

\*Fragrance Ingredients Index 2002. Givaudan S. A.

15 Adding 1-cyclooct-3-enylethanone to the fragrance composition significantly increases the diffusion of the whole fragrance, offering a better base coverage of the soap. 1-cyclooct-3-enylethanone adds a sophisticated agrestic note in the range of Armoise oil, with ozonic, cucumber undertones. It also imparts more volume to the woody accord.

# Claims

1. The use of a compound of formula I as fragrance,

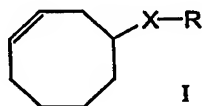


wherein X is carbonyl, or  $-(\text{CHOH})-$  ; and

R is methyl or ethyl, or linear or branched C3 to C5 alkyl; or

R is vinyl or linear or branched C3 to C5 alkenyl.

2. The use of a compound according to claim 1 selected from the group consisting of 1-cyclooct-3-enylethanone, 1-cyclooct-3-enylpropan-1-one, 1-cyclooct-3-enyl-2-methylpropan-1-one and 1-cyclooct-3-enylpropan-1-ol.
3. The use of a compound as defined in one of the claims 1 or 2 in fragrance applications.
4. A fragrance application comprising a compound as defined in any of the claims 1 or 2, or a mixture thereof.
5. A fragrance application according to claim 4 wherein the fragrance application is a perfume, household product, laundry product, body care product or cosmetic.
6. A compound of formula I



wherein X is carbonyl, or  $-(\text{CHOH})-$  ; and

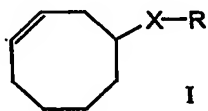
R is methyl or ethyl, or linear or branched C3 to C5 alkyl; or

R is vinyl or linear or branched C3 to C5 alkenyl;

provided that when X is carbonyl, R is not methyl.

**Abstract**

This invention relates to cyclooct-3-enes of the formula I, wherein X and R are defined in the specification.



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